ORGANIC PHOTOVOLTAIC DEVICES INCORPORATING NANOSTRUCTURES IN THE PHOTOACTIVE LAYER: TOWARDS CLEAN SOLAR ENERGY GENERATION

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Abstract

In this article we report the nanostructures formation in the thin films of several organic semiconductors. The thin films have been deposited onto glass substrates by a solution processable of spin-coating technique. The nanostructures are obtained by applying a simple surface solvent treatment process either by soaking or solvent vapor treatment. The influence of solvent treatment on the surface morphological properties has been investigated via a surface profilometer, absorption spectroscopy, X-ray Diffraction Spectroscopy and Atomic Force Microscopy (AFM). It reveals that the spin-coated TsCuPc thin films have nano-structures as evident from the surface profile image, which then confirmed by AFM image. Besides, the polymer chains have been re-organized after solvent treatment and the crystallinity is increased. Such crystalline increment provides a better pathway for charge carrier transport. The photovoltaic performance has improved to some extent for the device containing nano-structured film. We infer this enhancement is due to a larger interface area for exciton dissociation to generate free charge carriers of electrons and holes within the nanostructured film.

Keywords: Organic solar cells, photovoltaic, organic semiconductors, thin films, nanostructures.

1. Introduction

The world demand on energy is increasing; on the other hand the fossil fuel is getting depleted day by day and creating a huge amount of green-house effect as well as carbon-based pollution. Therefore, finding an alternative source of reliable renewable energy source is the prime importance task. Solar photovoltaic technology can provide a real alternative to fossil fuel generated energy. The photovoltaic system acts as one of the most economical ways to fulfill our energy requirements efficiently, since the sun-light is abundant in nature and free. The generated solar energy will be free of carbon pollution and green-house gases. However, the major problem of commercially available solar panels is the price; they are very expensive. Organic photovoltaic (OPV) devices containing organic, polymer or dye semiconductor materials [1-4] have received considerable attention as a third generation after silicon-based in the first and second generation solar technologies. These are due to their attractive benefits by offering a simpler device structure, easier fabrication process and the prospect of lower manufacturing cost as compared to the current inorganic silicon solar panels [1,2]. The required thickness of the photoactive layer made from organic semiconductors is within a range of 100 to 300 nm only, which is much lower compared to those required of about 2 μm for amorphous and 300 μm for crystalline silicon cells. Hence, the lower material consumption would signifantly reduce the overall production cost. Nevertheless, the power conversion efficiency of OPV devices is still much lower than that of their inorganic counterparts and one of the constrain is due to the low charge carrier mobility in most organic materials.

Organic semiconductors are characterized by π-π conjugated bonding, i.e. alternating single and double bonds. Generally, the highest mobility occurs along the π–π conjugated direction. Hence morphologically controlled organic semiconductors play a crucial role in determining characteristic features of the charge carrier generation and charge transport [5-11]. For example, a standing-up arrangement of organic semiconductor molecules show high charge mobility in a direction parallel to the substrate surface [7]. Usually, the morphology of the organic thin films may be tuned by exploiting the ratio of donor and acceptor weight ratio [8] and the choice of solvent [8,9]. Then, these thin films can be further improved morphologically by employing thermal or solvent post-annealing processes [10,11].

In our research studies, we focus on solution processable of organic semiconductors which can be spin-coated to form uniform nano-scale thin films. This method provides a simple technique of film deposition as well as cost-effective. Formation of nanoscale texture or film morphology of the organic semiconductors layers can dominates the performance of the device being optimized in our laboratory. In this report, the objectives of our

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research work are; (i) to study the formation of nano-structured organic layer by applying a simple method of solvent treatment and (ii) to investigate the influence of morphological properties on the performance of the organic photovoltaic devices.

2. Eperimental Methods

The organic semiconductor of nickel(II)-phthalocyanine-tetrasulfonic acid tetrasodium salt (TsNiPc), polymer (P3HT), (PCBM) and were purchased from Sigma-Aldrich and used without further purification. The chemical structures of materials are shown in Figure 1(a), (b) and (c). There were two parts of the experiments; in the first part, we produced TsNiPc films of treated and untreated with a poor toluene solvent onto glass substrates. Thin film of photoactive layer of TsNiPc was deposited onto the glass by spin-coating this material solution in de-ionized water. The solvent treated film was performed by soaking the film into toluene solvent for 20 minutes and let it dried under ambient condition. In the second part of the experiment, the mixture of P3HT:PCBM films (weight ratio 1:1) have been deposited onto glass substrates by spin-coating the materials solution in a co-solvent of di-chlorobenzene/chloroform (1:1) and the preparation of this thin film was reported previously [9]. Then we applied a method of solvent vapor treatment on the P3HT:PCBM film [11], where the thin film samples were placed for 1 hour inside a covered area. We used a big beaker as a cover and a small beaker as a container, filled with diclorobenzene/chloroform co-solvent. Then, the samples were taken out and annealed on a hot plate at 150 ^{o}C to remove the residual solvent. The surface morphology properties of the films were investigated by an Atomic-Force-Microscopy (AFM). The Absorption spectra of thin films were measured using Jasco Model V-570 UV-VIS-NIR Spectrometer. A Siemens D5000 X-ray diffractometer was used to record the X-ray diffraction (XRD) patterns.

For solar device fabrication, the commercial indium-tin oxide (ITO) glass substrates with a sheet resistance of 7Ω/square were used as the bottom electrode. Then, the organic photoactive films were deposited by spin-coating onto ITO electrode and then subjected to solvent treatment as previously explained. Finally, the top aluminium (Al) electrode was deposited using a thermal evaporator under high vacuum of 10^{-5} mbar. The schematic diagram of the device construction of ITO/photoactive organic layer/Al is illustrated in Figure 1(d). The current-voltage characteristics of the devices were measured using a Keithley 2400 Source Measuring Unit in the dark and under the AM1.5G-filtered light irradiation at 100mW/cm^2 from an Oriel solar simulator. The final device construction of organic semiconductor based solar cell is shown schematically in Figure 1(a). The light source was illuminated through the transparent ITO electrode. The thickness of the photoactive films was measured using a surface profiler meter.

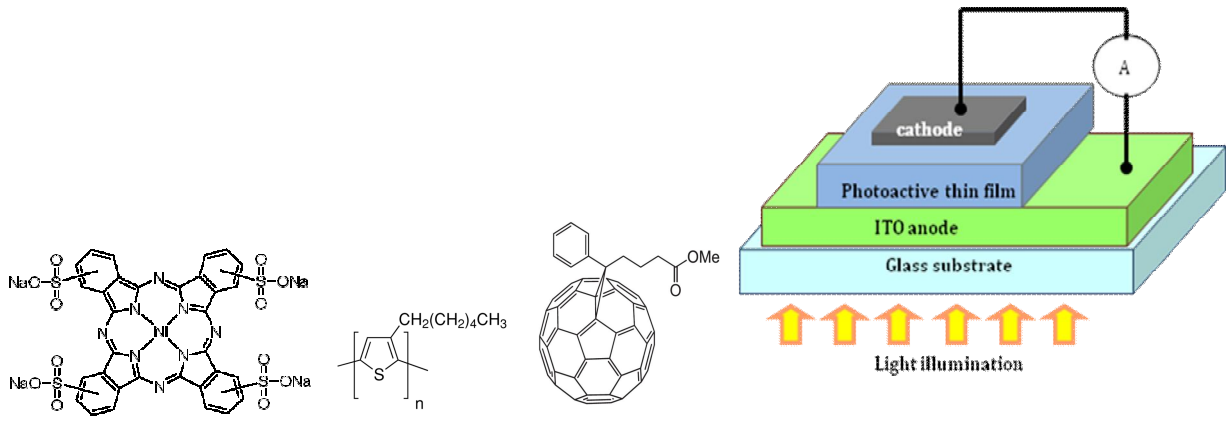


Figure 1. (a) The schematic diagram of the solar device incorporating organic semisonducting materials as the photoactive thin film; The chemical structures of (b) TsNiPc; (c) P3HT and (d) PCBM.

3. Results and Discussion

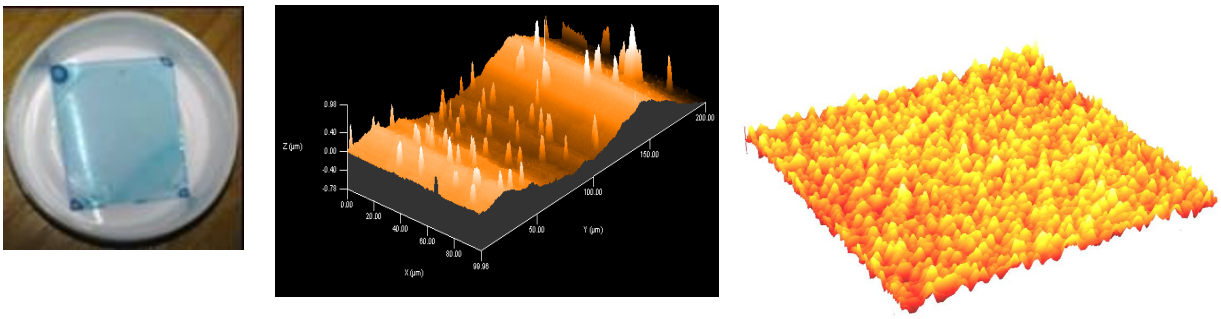
3.1. Nanostructures in TsNiPc thin films.

TsNiPc is an example of small molecular weight organic semiconductors. In many cases, thin films from the small organic molecules cannot be deposited by spin-coating method due to poor solubility of material in solvent. However, here we successfully produced a homogenous blue-colored TsNiPc thin film by spin-coating from a water

solution as shown in Figure 2(a). In our previous reports, we also managed to form homogenouos and smooth organic films using spin-coating technique based on the small molecular weight organic semiconductors of tri-phenylamine derivatives [12] and tris (8-hydroxyquinolinate) gallium and aluminum organometallic materials [13].

In order to create nano-structures using a solvent soaking method, we need to find the suitable poor solvent without dissolving the whole organic film from the glass substrate. After trying to soak in many types of solvent, we found that this TsNiPc film does not dissolve in toluene. On the other hand, by soaking this film into toluene for 20 minutes, some upper part of the TsNiPc film has been slowly removed from the film. Upon this treatment, spike-like nanostructures were formed as observed in the 3D images of surface profiler in Figure 2(b). In our observation, we found that the surface profilometer may be used as a preliminary tool in visualizing the morphology of organic semiconductor films. Figure 2(c) of AFM image of the treated TsNiPc film, confirmed the nanostructure formation compared to a smoother film for the untreated film (AFM image of the pristine sample is not shown here). From these results, we infer that large surface roughness can be achieved by employing a solvent soaking method, which is essential for providing large interface area in organic semiconductor thin films. By soaking the organic semiconductor film in a poor solvent of chloroform, allows solvent molecules to interact with the organic upper layer. This interaction leads to molecular reorganization, hence forming of nanostructured organic film.

The fabrication of solar cells based on this treated TsNiPc film is still on-going process, and the results will be published elsewhere in near future. We believe these nanostructures would enhance the performance of photovoltaic device containing such feature in the photoactive layer due to the larger interface area. The generation of free charge carriers from excitons (bound electron-hole pairs) can be improved through the formation of larger interface area in nanostructured film [14]. The researchers reported that nanostructures can be formed in copper phthalocyanine (CuPc) by employing a facile method of solvent dropping onto film surface [14]. This CuPc film was formed via a thermal evaporation technique which is known as a dry method of film deposition. We have been trying to avoid using this evaporation method for film deposition due to a rather complicated technique and a larger amount of material required as comparison to a simple spin-coating method.



(a) (b) (c)

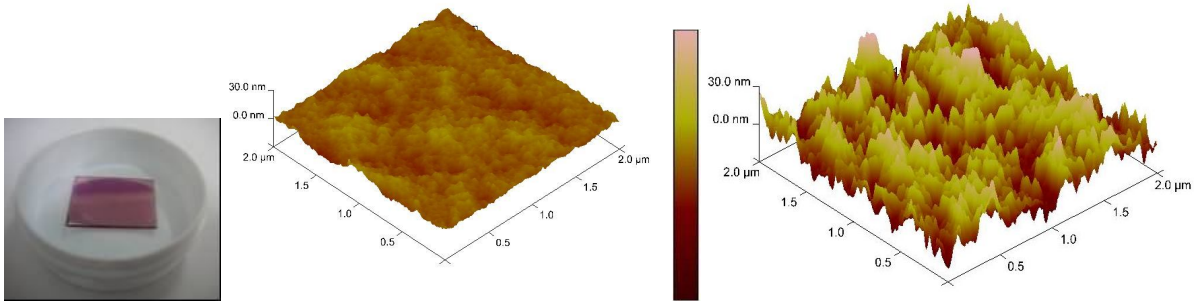
Figure 2. (a) A photo image of TsCuPc film spin-coated on glass; (b) The 3D surface profilometer image of a TsCuPc film with 200 X 100 micron and 100 nm heights; and (c) AFM image of the TsCuPc nanostructured film for solvent treated showing film with spikes (AFM images with the size of 40 x 40 micron and 100 nm height).

3.2 Nanostructures in polymeric based solar cells.

A smooth and homogenous blend films can be formed by spin-coating the polymeric based materials of P3HT:PCBM from a co-solvent of dichlorobenzene onto glass substrate as shown in Figure 3(a). The thickness of the polymer thin films was approximately 120 nm. In this second part of the study, the thin films were subjected to a solvent-vapor annealing method. In this method, the solvent molecules evaporated slowly from the polymer thin film, due to a vapor dense atmosphere inside the beaker where samples have been placed. By exploiting this technique, we managed to create a slower speed of solvent-removal. After all the solvent molecules were removed from the film by annealing at 150 ^{o}C, these treated samples revealed an interesting features. Figure 3(b) and 3(c) show the AFM images of the pristine (untreated sample) and treated sample, respectively. The surface roughness in the pristine film was measured to be around 3 nm whereas in solvent-treated sample was 15 nm. This significant rise in the surface roughness indicates the chain ordering inside the polymer is improved, possibly because slow evaporation of the solvent enables slower growth of films.

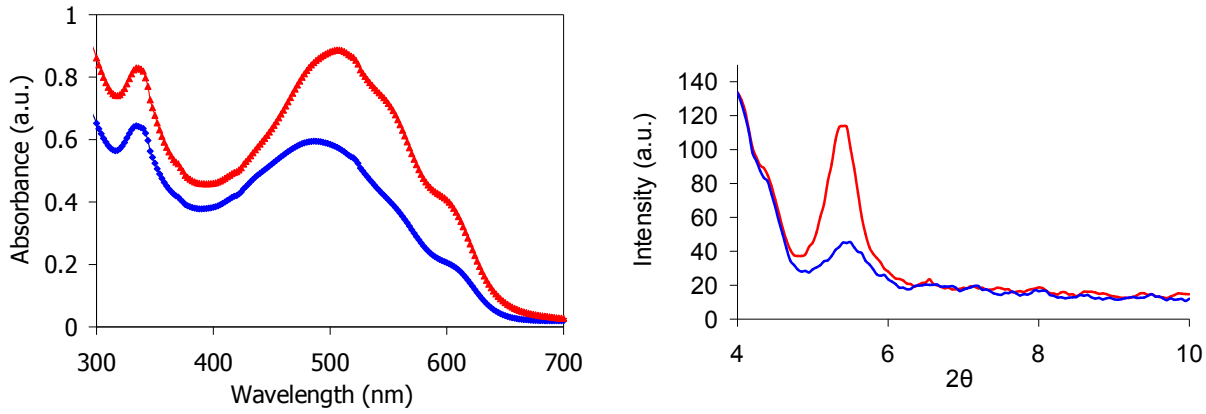
The influence of this re-organization of polymer film can be observed via absorption spectra as shown in Figure 4(a). We assign the higher absorption within the treated film (red colored curve) is associated with higher portion semi-crystalline phase and a better polymer chain ordering of the film. The better crystallization in the treated film is then proved in XRD spectra, shown in Figure 4(b). The XRD results are consistent to our observation

in the absorption spectra. The higher intensities in both spectra of absorption and XRD, indicate that the slow solvent treatment process plays important and simple method in improving materials structure and molecular ordering of organic semiconductor films.



(a) (b) (c)

Figure 3. (a) AFM image of the pristine film; (b) AFM image of the solvent vapor treated P3HT:PCBM. (AFM with the size of 2 x 2 micron and height is 30 nm for both cases).



(a) (b)

Figure 4. Influence of solvent treament on P3HT:PCBM mixture film on (a) absorption spectra and (b) XRD spectra. The pristine sample is shown by the red colored curve and the treated sample is shown by the blue colored curve.

3.2. Photovoltaic Properties of a selected organic solar cell.

Electrical characteristics of the organic solar cells fabricated from the treated photoactive layer of P3HT:PCBM were measured under light illumination of 100 mW/cm^2. The influence of nanostructure formation inside the photoactive layer has been compared by measuring the electrical behaviour in both pristine and nanostructure devices. In the pristine device, the untreated photoactive layer was used, whereas we employed the treated film in the nanostructure device. The current density-voltage (*J-V*) characteristics of the pristine device containing the untreated film and the nanostructured device containing solvent treated film are shown in Figure 5. It can be seen from the *J-V* curve, the shunt resistance has been lowered for the nanostructure device (red colored curve) which may result in a decrease in open-circuit voltage, *V*oc. In contrast, the device containing nano-structures in the photoactive layer show short-circuit current, *J*sc about five-times higher compared to the pristine device. In general, our organic solar photovoltaic cells can be improved from 0.002 % to 0.4% conversion efficiency by utilizing a nano-structured photoactive layer. Our organic photovoltaic devices were prepared in ambient air without employing any encapsulation process, thus the device degradation occurred very fast. The encapsulated organic devices are still in the process of fabrication, and the results will be published elsewhere.

The photovoltaic performance particularly on the photocurrent has improved to some extent for the device with treated film by improving the conductivity via nano-structure formation on the organic semiconductor surface.

This AFM images results indicate that morphology of the organic film plays important role in the charge transfer process. The nano-structured films provide large interface area for charge carrier generation and assist in charge transport. Larger interface area creates a better pathway for charge carriers to reach the external electrodes, leads to the enhancement in the photovoltaic performance.

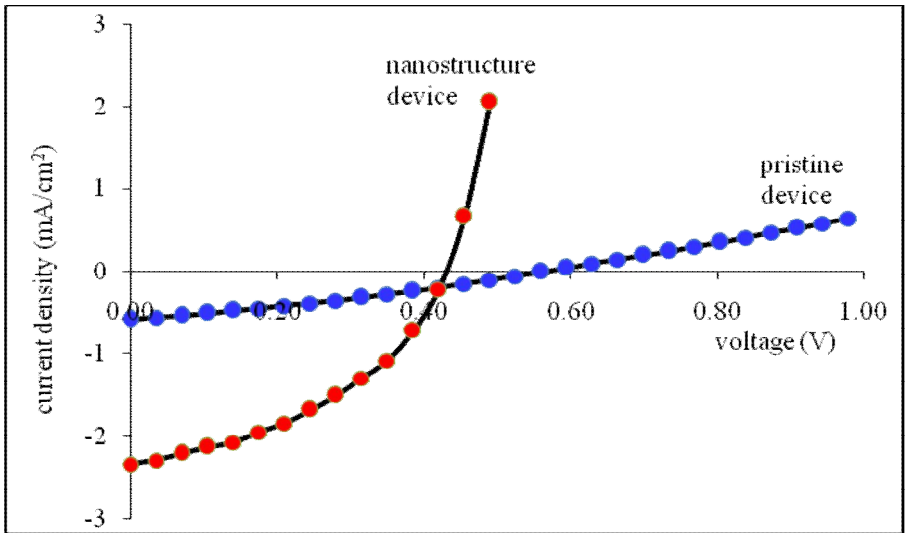


Figure 4. Influence of solvent treament on P3HT:PCBM mixture film on . The pristine sample is shown by the red colored curve and the treated sample is shown by the blue colored curve.

4. Conclusions

We have investigated the influence of solvent treatment on the formation of nanostructure of the organic semiconductor thin films. A few drop of solvent particularly with higher boiling point, can induce morphology self-organizing of the organic film surface into ordered molecular structure. This formation of nano-structures leads to enhanced photoconductivity in the photovoltaic solar device. Even tough, the efficiency of the organic-based photovoltaic solar cells is still very low, but the future prospect of these devices is very promising and bright towards generating clean energy. Several steps have been taken into account for further research works including device encapsulation process in order to improve the efficiency of the organic-based photovoltaic devices.

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